

CONTINUOUS REMOVAL OF SULFUR OXIDES AT AMBIENT TEMPERATURE, USING ACTIVATED CARBON FIBERS AND PARTICULATES

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INTRODUCTION

The control of sulfur dioxide emissions from fossil fuel combustion and other industrial processes has been recognized as one of the major environmental issues, in both developed and developing countries. In the US, energy-intensive and space-consuming sorbent scrubbing processes that are widely used to remove SO₂ from flue gases also produce huge amounts of process wastes. The management and disposal of the by-product wastes by landfill not only represent poor resource utilization, but can cause further environmental and land use problems.

Activated carbons have offered alternative technologies for the clean-up of flue gas streams. A dry process for the simultaneous removal of sulfur and nitrogen oxides has been commercialized by Mitsui - Bergbau Forschung, using granular activated carbons[1]. Carbon is lost in this process by chemical reaction and by attrition, and to supplement this loss accounts for about half of the process operating cost. In addition, high capital costs are associated with the large reactor volumes and the systems to transport granular carbons in moving bed operations, and have provided obstacles to the wide-scale development and use of the process.

In the early 1970s, studies were made of the continuous oxidation and hydration of sulfur dioxide over granular activated carbons in a trickle bed, with the desorption of sulfuric acid by flowing water in the same reactor [2]. Similar concepts of water desorption have been also proposed for the regeneration of activated carbons [3]. An important feature of these methods is that sulfur species are converted to useful chemicals in the form of sulfuric acids. However, the wet desulfurization process is limited by slow rates of oxidation and mass transfer through liquid phase. Improvements have been recently made to increase process effectiveness and to obtain high concentration sulfuric acid, including cyclic operation of trickle beds, higher reaction temperature (at 80 °C rather than ambient temperature) and the loading of platinum on activated carbons [4,5]. A combined process that also removes NO_x has been proposed through selective catalytic reduction (SCR) with ammonia in a separate unit, possibly using a different activated carbon catalyst [5]. On the other hand, Mochida and his coworkers at Kyushu University, Japan, have found that activated carbon fibers (ACF) produced commercially from polyacrylonitrile (PAN) are very effective catalysts for the continuous removal of SO₂ from humidified model flue gases [6,7]. These and other commercial activated carbon fibers have also exhibited activity for NO oxidation into NO₂ at ambient temperature [8].

For the past few years, we have been investigating the synthesis of general purpose carbon fibers and activated carbon fibers from different isotropic pitch precursors [9,10,11]. In collaboration with the Japanese researchers, we have found that certain fibers that we have synthesized in the laboratory are very active for the oxidation of SO₂ and NO [12]. The results were so encouraging that we constructed a reaction system to make further investigations. In this paper, we describe the performance of activated carbon fibers and particulate activated carbons for the continuous removal of SO₂. The effects of heat treatment, particle size, and several basic engineering parameters of the catalyst bed were also examined.

EXPERIMENTAL

Comparisons of catalytic activities for SO₂ conversion were made using three different types of activated carbon fibers and a commercial granular activated carbon in two particle size ranges. The activated carbon fibers were produced from coal-tar pitch (a commercial product from Osaka Gas Co.) and synthesized in this laboratory from shale oils and coal liquids (The details of the preparation procedure have been described elsewhere [9,10]). The granular activated carbon (BPL type, Calgon Corp.) was produced from bituminous coals and was selected for the study because this material has been already tested in model flue gas-water systems for SO₂ oxidation [4,5,13,14]. Different particle size ranges were obtained by grinding and sieving. The properties of the activated carbon fibers and particles are summarized in Table 1. Their BET surface areas are varied from 980 to 1060 m²/g. The activated carbon samples were either used directly or after heat treatment in nitrogen at 800 °C for 1 hour.

Figure 1 shows a schematic of the reaction system. The flow of dry gases from cylinders were metered by mass flow controllers (MFC) into a mixing chamber. Water was added to the gas mixture exiting the mixing chamber, by passing a stream of air through a water bubbler that is maintained at constant temperature. The combined gas mixture was fed to reactor at a flow rate that can be varied from 100 to 3000 ml/min. A tubular glass reactor (typically, $\phi 8 \times 110$ mm) was equipped with a insulating jacket for liquid media to be circulated to maintain a stable reaction temperature. The catalyst bed dimensions can be altered through exchanging different size tubular reactors. The SO_2 concentration in the gas stream was monitored continuously with an infrared analyzer. The reactor exit gas was passed through a liquid collector and an ice trap before entering the SO_2 analyzer in order to reduce the water vapor pressure to a low and steady level. The liquid products from the reactor were drained into the liquid collector.

RESULTS AND DISCUSSIONS

Both fiber and particulate activated carbons in their as-received forms exhibited measurable activity for the oxidative removal of SO_2 from the simulated flue gas, Figure 2. In each case, after a short time on stream, SO_2 was detected in the effluent gases and increased in concentration to a steady value. The steady-state removal (SSR) of SO_2 is dependent upon the type of activated carbon. The shale oil-derived fibers showed the highest activity, with 60% SO_2 removal at steady state. This result is consistent with our earlier findings [12]. The Osaka Gas fibers had much lower activity as observed by the Kyushu University group [7], and were comparable to the performance of some granular carbons. The much higher activity of the shale oil fibers is believed to be related to their high nitrogen content (coal-tar pitch fibers ~0.5 wt% versus >2.5 wt% for shale oil products), although the specific role and form of the nitrogens is not understood.

It is to be noted that the activity of the granular carbons is significantly increased upon reducing the particle size. This indicates the importance of mass transfer limitations in the reaction process and that these can be reduced by using smaller particle sizes. In practical terms, a catalyst bed consisting of fine particle activated carbons would give a high pressure drop, especially in the two-phase flow regime where sulfuric acid is draining through the bed. By utilizing activated carbon fibers in some suitable arrangement (other than loosely packed), the advantages of reducing mass transfer effects could be realized without the attendant penalty in pressure drop. The open pore structure of fiber beds would facilitate fast contact with the reaction surfaces contained in 10 - 20 microns filaments and assist liquid drainage.

Figure 3 shows the effects of prior heat treatment on the catalytic activities of both particulate and fiber activated carbons. Heat treatment has been found to be effective for improving the catalytic activity of commercial PAN and coal tar pitch-based activated carbon fibers [6,7,8]. At equivalent loading, the activity of the fibers decreased in the order, shale oil >> coal liquids > coal tar pitch (Osaka Gas fiber). As in Figure 2, the small particle granular carbon is somewhat more active than the Osaka Gas fibers, although at double the loading. A comparison of Figures 2 and 3 shows that the pretreatment procedure greatly increased the steady state activity of the shale oil fibers, from 60 % to about 90 % SO_2 removal. It can be seen that at high loading, 100% steady state removal was achieved with heat-treated shale oil fibers and this activity was maintained for at least 72 hours. In contrast, the extent of activity improvement is smaller for Osaka Gas fibers and the small particle BPL carbons.

Table 2 summarizes the typical reaction conditions and parameters of the catalyst beds for the two forms of activated carbons: shale oil fibers and small particle granules. Because of the low density of the fibers, only half the weight of the particulate activated carbons can be packed in a similar volume. With a reactant gas flow rate at 200 ml/min, space velocities of 10380 and 9180 h^{-1} were obtained for the activated carbon fiber and particle beds, respectively. Under these conditions, about 90 % SO_2 removal was achieved, using heat-treated shale oil fibers with a bed depth of only 23 mm (Figure 3). Complete removal of SO_2 was obtained by the activated fiber bed 46 mm deep, with a corresponding space velocity of 5180 h^{-1} . In contrast, using a trickle bed reactor with granular activated carbons, a few meters depth would be needed to achieve 95% SO_2 removal at velocity of from 1000 to 2850 h^{-1} [15]. The high rates of mass transfer and reaction over activated carbon fibers would permit the treatment of high SO_2 content flue gases and production of more and high-concentration sulfuric acids as by-product.

SUMMARY

The catalytic performance of fibrous and particulate activated carbons obtained from different precursors was investigated for SO_2 removal at ambient temperature, using a humidified model flue gas. Despite their similar BET surface areas, activated carbon fibers prepared in the laboratory from shale oil and coal liquids were found to exhibit much higher activity than a

commercial activated carbon fiber produced from coal tar pitch. This confirmed our early findings. It is considered that the high nitrogen content of the shale oil fibers is an important contributor to their high activity. However, the form of nitrogen species, and the nature and the role of the surface groups are not yet understood. Comparisons between activated carbon fibers and particulates indicate that the small dimensions (a couple of tens of micron diameters) of the fibers is a key factor to realizing the full catalytic potential for this application, because of high mass transfer resistance in the gas-liquid-solid system. Carbon fiber beds can provide an open pore structure through which reactants and products in both gas and liquid phases can flow to reach and to interact with the surfaces of carbon catalysts.

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Table 1 Properties of Activated Carbon Catalysts

Sample ID	Type	Size*(μm)	BET Surface area (m^2/g)	Precursor
AF-SK25	fiber	6 - 16	986	shale oil
AF-CE	fiber	8 - 18	1013	coal liquid
AF-O10	fiber	8 - 20	1057	coal tar
BC2060	particle	200 - 600	1048	coal
BC6012	particle	600 - 1200	1020	coal

* Diameter for fibers or particles

Table 2 Comparison of reaction conditions and SO_2 removal for activated carbon fibers and particles

AC type	fiber	particle
Catalyst bed:		
AC ID ^{a)}	AF-SK25	BC2060
Weight (g)	0.25	0.50
Diameter (mm)	8	8
Depth (mm)	23	26
Volume (cm^3)	1.16	1.31
Temperature ($^{\circ}\text{C}$)	30	30
Space velocity ^{b)} (h^{-1})	10380	9180
Steady state removal ^{b)} (%)	89	19

a) Samples heat-treated at 800°C for 1h in nitrogen.

b) Reactant gas at 200 ml/min: SO_2 1000 ppm, O_2 5 vol %
 H_2O 10 vol %, N_2 balance.

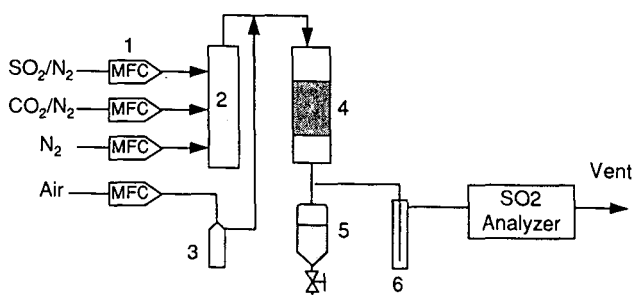


Figure 1 Schematic of reaction system for evaluation of SO_2 continuous removal at ambient temperature:

1, Mass flow controller; 2, Mixing chamber; 3, Water bubbler;
 4, Reactor; 5, Liquid product collector; 6, Ice trap

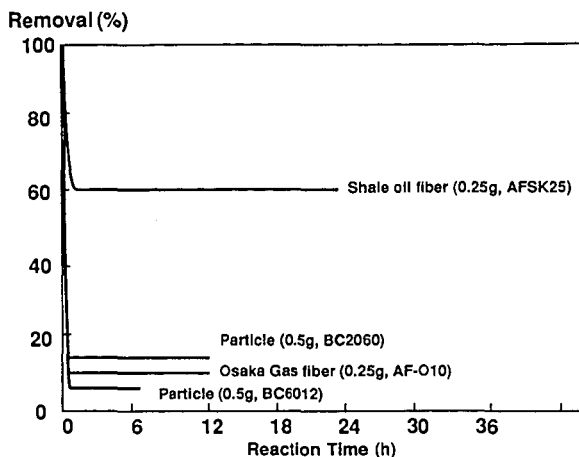


Figure 2 Activity of as-received activated carbons for SO_2 removal at 30 °C;
Reactant gas: 200 ml/min, 1000ppm SO_2 , 5 vol% O_2 , 10 vol% H_2O in N_2

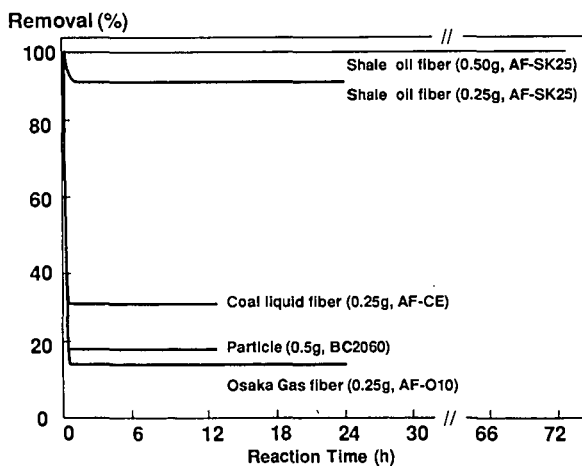


Figure 3 Activity of heat-treated activated carbons for SO_2 removal at 30 °C;
Reactant gas: 200 ml/min, 1000ppm SO_2 , 5 vol% O_2 , 10 vol% H_2O in N_2
Heat treatment: 800 °C, 1 h, in nitrogen